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# Differentiation Using Microwave Plasma Torch Desorption Mass Spectrometry of Navel Oranges Cultivated in Neighboring Habitats

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Supporting Information

**ABSTRACT:** The molecular fingerprinting of intact fruit samples combined with statistical data analysis can allow the assessment of fruit quality and location of origin. Herein, microwave plasma torch desorption ionization mass spectrometry (MPT-MS) was applied to produce molecular fingerprints for the juice sac and exocarp of navel oranges cultivated in three closely located habitats, and the mass spectrometric fingerprints were differentiated by principal component analysis (PCA). Because of the relatively high temperature and high ionization efficiency of MPT, the volatile aroma compounds and semivolatile chemicals in the navel oranges were sensitively detected and confidently identified by collision induced dissociation (CID). The limit of detection (LOD) of MPT-MS for vanillin was 0.119 $\mu$g/L, with the relative standard deviation (RSD, $n$ = 10) of 1.7%. The results showed that MPT-MS could be a powerful analytical platform for the sensitive molecular analysis of fruits at molecular level with high chemical specificity, allowing differentiation between the same sorts grown in neighboring habitats.

**KEYWORDS:** *microwave plasma torch, ambient mass spectrometry, desorption ionization, navel orange, principal component analysis*

## INTRODUCTION

Navel orange is a common commodity of citrus containing more than 130 beneficial compounds with high nutritional and medicinal value to humans.[1] Recent studies have reported that sugars are mainly found in juice sac,[1] and ketones, alkenes, flavonoids, glycosides, and other volatile flavor compounds are mostly contained in the exocarp.[2,3] Although the appearance of navel oranges from different habitats is similar, the quality, nutrients, and tastes could be significantly different due to the difference in cultivation and planting environments, which are likely to cause the molecular diversity of the active metabolites as well as the nutritional value of navel oranges.

Currently, analytical methods such as infrared spectroscopy (IR),[4,5] gas chromatography−mass spectrometry (GC−MS),[6−8] high performance liquid chromatography (HPLC),[9−11] and liquid chromatography−mass spectrometry (LC−MS)[12] are typically used for the quality inspection of navel oranges. These methods have a high analytical power but usually require complicated and time-consuming experimental procedures, which hinder high throughput sample analysis. Powered by the advent of direct ionization techniques including but not limited to desorption electrospray ionization (DESI),[13] desorption atmospheric pressure chemical ionization (DAPCI),[14,15] extractive electrospray ionization (EESI),[16] internal extractive electrospray ionization (iEESI),[17] direct analysis in real time (DART),[18] and microwave induced plasma (MIP),[19] the speed and simplicity of mass spectrometric analysis have dramatically improved. In ambient MS, molecules that are easily protonated/deprotonated can be sensitively detected by ambient ionization techniques such as DESI, EESI, and LAESI,[20] which produce analyte ions in a way similar to ESI. It was reported that compounds of weak polarity could be sensitively detected by DAPCI,[21] LTP,[22] and many other ionization methods based on ambient corona discharge.[23] However, the volatile fragrance compounds of navel oranges produce similar MS fingerprints, and different kinds of navel oranges are difficult to distinguish using a sensory method. Therefore, a technique with high desorption and ionization energy would be of interest, because such a technique could provide rich molecular information on the compounds, which are unlikely to be detected by commonly available soft desorption ionization methods.

Microwave plasma torch (MPT),[24] normally used as the excitation source for optical emission spectrophotometry, was employed in analytical mass spectrometry as the ionization source characterized by its relatively high temperature for easy desorption and highly abundant ionic species for effective ionization. So far, MPT-MS has been applied to trace analysis of ambient samples in life sciences, food safety, and public security.[25−27] In this study, MPT-MS was used to directly record the characteristic MS fingerprints of the juice sac and exocarp of navel oranges. The MS data were then subjected to principal component analysis (PCA),[28] which resulted in sensitive differentiation of navel oranges cultivated in three closely located habitats, because MPT-MS provided rich

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molecular information on the compounds due to its high desorption and ionization energy.

## MATERIALS AND METHODS

**Reagents and Materials.** The microwave generator (WGY-20, 2450 MHz) and microwave plasma torch tube were provided by Changchun Jilin Little Swan Instruments Co. Ltd. (Changchun, China). Chemicals such as methanol (A.R. grade) and standard substance such as 5-hydroxymethyl furfural, vanillin, and 1-nonanol were bought from Chinese Chemical Reagent Co. Ltd. (Shanghai, China). Ultrapurity argon (>99.99%) was purchased from Jiangxi Guoteng Gas Co. Ltd. (Nanchang, China).

Navel oranges (cv. 'Newhall') were collected from three closely located habitats, which were geologically positioned within 3 km in the naturally formed farming valleys (Guoxi, Anxi, and Fengxi) at Yongfeng Town, Xingguo County, Jiangxi Province. The navel orange trees were 12 years old. The orchard managements were under the same planting standard for navel oranges. The navel oranges located at the southern and upper parts of the tree with similar sizes were harvested on the same day. Prior to analysis, the dust on the orange surface was washed off by distilled water at room temperature. The juice sac samples were cut from randomly selected navel oranges, but a total of 72 exocarp samples were directly sampled by the MPT around the maximal circle of the navel orange. For better comparison, each piece of the juice sac (72 samples) was cut into 10 × 10 × 3 $mm^3$.

**Experimental Method.** All of the experiments were carried out using a LTQ-XL linear Ion trap mass spectrometer (Finnigan, San Jose, CA) coupled with a microwave plasma torch (Changchun Jilin University Little Swan Instruments Co., Ltd., Changchun, China). A SC102 stepper motor (Beijing Optical Century Instrument Co., Ltd., Beijing, China) provided a mobile platform to hold the sample for analysis.

For MS analysis, the MPT device was slightly modified from the original configuration for atomic emission spectrophotometry described elsewhere.[29−32] The vertical distance ($h$) between the sample surface and the plasma torch was 8 mm. The angle ($\alpha$) between the microwave plasma torch and the sample surface was about 40°. The assembly of the MPT was carefully positioned to be coaxial with the ion entrance capillary of the LTQ mass spectrometer, allowing a distance ($d$) of 10 mm between the ion entrance and the MPT (Figure 1). The microwave power was 50 W. The reflected microwave power was minimized to reach 0 W by adjusting the pipe pistons of the microwave plasma torch. The flow rate of working gas (Ar) was 300 mL/min, and the flow rate of the carrier gas (Ar) was 800 mL/min. The positive ion detection mode was used to record the mass spectra, with the mass range of $m/z$ 50−1000. The LTQ-XL instrument was operated under the following conditions: the capillary temperature was 150 °C, the capillary voltage was 16 V, the tube lens voltage was 75 V, and the maximum ion injection time was 100 ms. For collision induced dissociation (CID) experiments, the mass-to-charge ratio window width of 1.2 Da was used to isolate the precursor ions. The collision energy was 15−35%, and the collision time was 30 ms. The rest of the parameters were automatically optimized by tuning the LTQ-MS instrument.

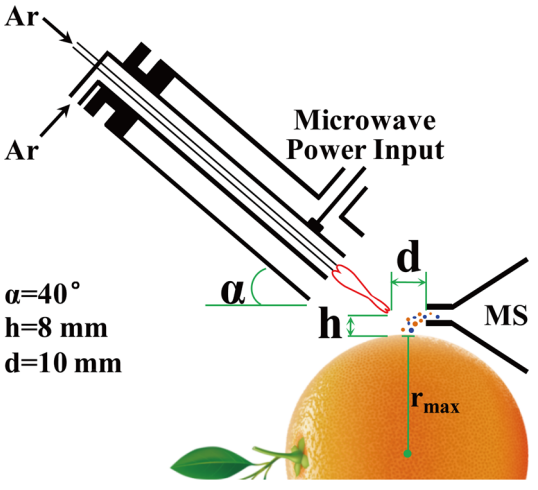


**Figure 1.** Schematic illustration of microwave plasma torch mass spectrometry for navel orange analysis.

## RESULTS AND DISCUSSION

**MPT-MS Analysis of Navel Orange Juice Sac Samples.** The MS fingerprints of juice sac samples were directly recorded using MPT-MS under the experimental conditions. Figure 2

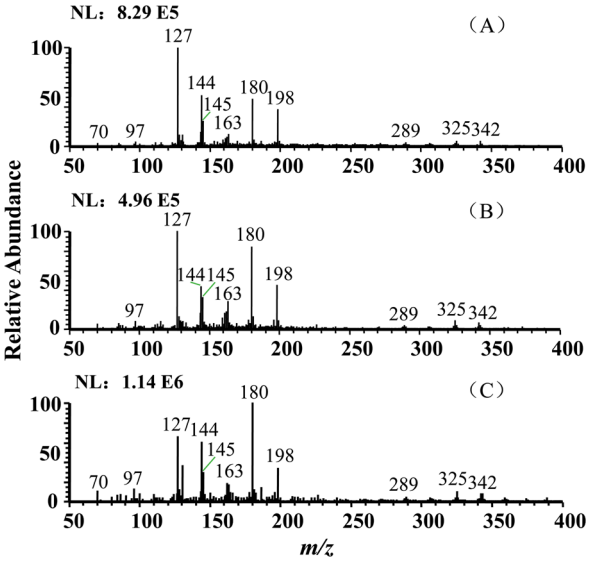


**Figure 2.** Fingerprint spectra of navel orange juice sac from three origins: (A) Guoxi, (B) Anxi, and (C) Fengxi.

shows the mass spectra of navel orange juice sac samples, with dominant peaks at $m/z$ 127, 144, 163, 180, and 198 and small peaks such as $m/z$ 289, 325, and 342. Apparently, the abundance of these peaks varied along with the juice sac samples, showing the correlation between the peaks and the habitats. The peak at $m/z$ 127 was tentatively assigned to protonated 5-hydroxymethyl furfural (5-HMF), **1** (Figure 3), which was favorably produced via degradation of the hexose during the heat-assisted desorption ionization process.[33−36] Upon CID, the precursor ion ($m/z$ 127) yielded characteristic fragments of $m/z$ 109 and $m/z$ 81 in the MS/MS spectrum (Figure 4A), probably by successive loss of $H_2O$ and CO. In the $MS^3$ spectrum of $m/z$ 127, the fragment ion at $m/z$ 81 was formed by the loss of $H_2O$ and CO. The fragmentation pattern was in good agreement with that generated using authentic 5-HMF, confirming that the $m/z$ 127 peak was due to 5-HMF. Note that less 5-HMF is normally found in normal navel orange tissue using ESI or low temperature ionization techniques (e.g., DAPCI, DESI, EESI); thus the 5-HMF was likely formed through the dehydration of hexose caused by extensive heating, due to the relatively high temperature of the MPT. Therefore, the intensity levels of 5-HMF ($m/z$ 127) served as the indicator of hexose, which also fluctuated along with the quality/flavor of navel oranges. In comparison with the previous study of metabolites in oranges (*Citrus sinensis*),[1] the abundant peak at $m/z$ 180 was assigned to $[glucosan+NH_4]^+$. Similarly, the assignment of peaks at $m/z$ 145 [glucosan−


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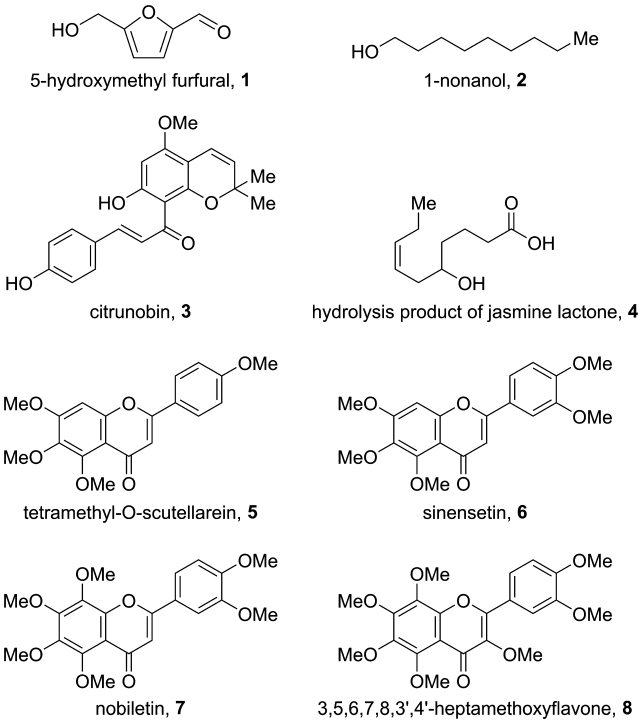


**Figure 3.** Chemical structures of 5-hydroxymethyl furfural, **1**, 1-nonanol, **2**, citrunobin, **3**, hydrolysis product of jasmine lactone, **4**, tetramethyl-*O*-scutellarein, **5**, sinensetin, **6**, nobiletin, **7**, and 3,5,6,7,8,3′,4′-heptamethoxyflavone, **8**.

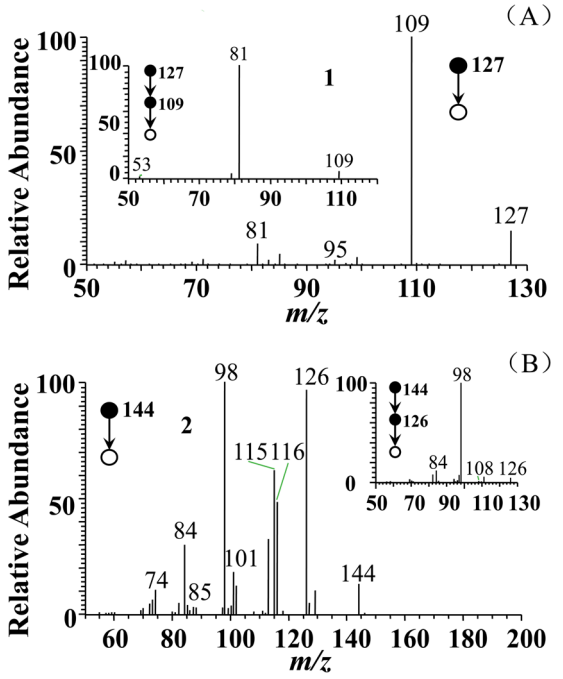


**Figure 4.** $MS^n$ spectra of the main substances of navel orange: (A) 5-HMF (inset: $MS^3$ spectrum of $m/z$ 127); and (B) 1-nonanol (inset: $MS^3$ spectrum of $m/z$ 144).

$OH]^+$, $m/z$ 163 $[glucosan+H]^+$, $m/z$ 198 $[hexose+NH_4]^+$, $m/z$ 289 $[2glucosan-H_2O-OH]^+$, $m/z$ 325 $[2glucosan+H]^+$, and $m/z$ 342 $[2glucosan+NH_4]^+$ were also enhanced, suggesting that the navel oranges were rich in sugar.[1,37] However, the relative abundance of these peaks varied notably for the navel orange samples from different habitats. Such differences in sugar levels could partially account for the difference in flavors.

Following the strategy for analyte verification, 1-nonanol (MW 144), **2** (Figure 3), a natural product found in navel orange, bitter orange, and many other plant essential oils, was also confidently detected from navel orange juice sacs. Upon CID, the protonated 1-nonanol ($m/z$ 144) generated major fragments of $m/z$ 126, 116, 115, and 98 (Figure 4B), by the loss of $H_2O$, $C_2H_4$, $C_2H_5$, and $C_2H_6O$, respectively. In the $MS^3$ spectrum of $m/z$ 144, the fragment ion at $m/z$ 98 was formed by the loss of $H_2O$ and $C_2H_4$. The CID fragmentation pattern was validated by using authentic 1-nonanol under the same experimental conditions.

**MPT-MS Analysis of Navel Orange Exocarp Samples.** MPT-MS was also applied for the direct fingerprinting of navel orange sample pericarp/exocarp, which minimized the potential damages to the fruit, so that the navel oranges could be normally traded as usual. The mass spectrometric fingerprints of exocarp from Guoxi, Anxi, and Fengxi are shown in Figure 5A–C, respectively, in which the main peaks at $m/z$ 153, 169, 186, and 353 were detected in every spectrum. However, the relative abundance for these peaks fluctuated considerably, according to the sample habitats. Apparently, the relative abundance of the peak at $m/z$ 353 recorded from Fengxi navel oranges (570 000 counts per second (cps)) was significantly higher than those either from Guoxi (265 000 cps) or from Anxi (226 000 cps) navel orange, making the Fengxi oranges outstanding from the other two. Upon CID, the protonated citrunobin, **3** ($m/z$ 353), produced major fragments of $m/z$ 338, 325, and 310, by the loss of $(-CH_3)$, CO, and $(-CH_3 + CO)$ (Figure 6A), respectively. In comparison with the previous study of metabolites in oranges (*Citrus sinensis*), the abundant peak at $m/z$ 353 was assigned to be protonated citrunobin,[1,38]

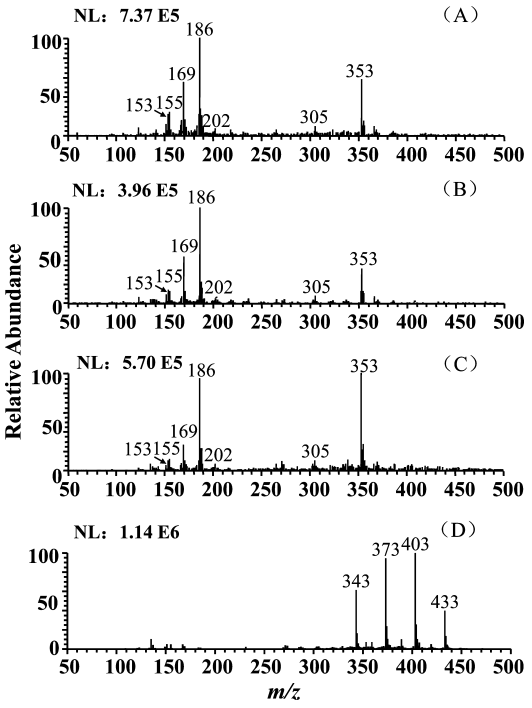


**Figure 5.** Fingerprint spectra of navel orange exocarp from three habitats: (A) Guoxi, (B) Anxi, (C) Fengxi, and (D) Fengxi exocarp heated for more than 30 s.


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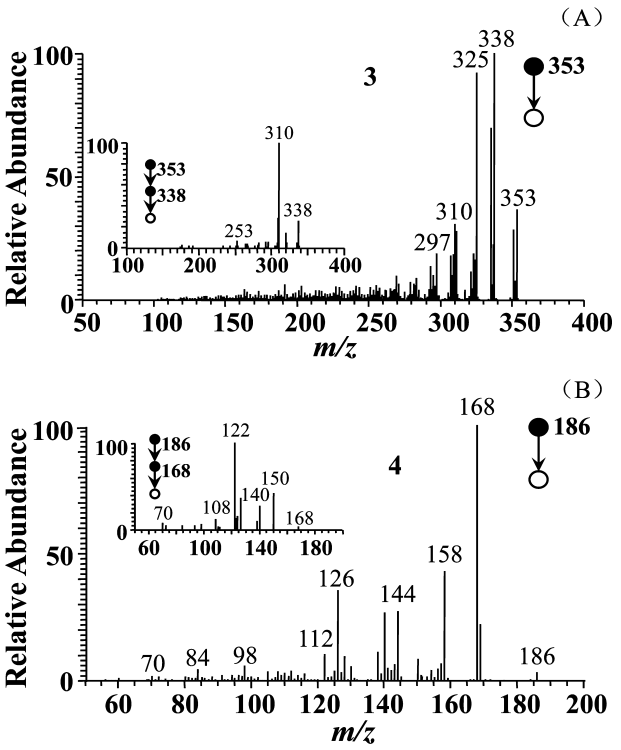


**Figure 6.** $MS^2$ spectra of the main substance of navel orange: (A) citrunobin (inset: $MS^3$ spectrum of $m/z$ 353); and (B) hydrolysis product of jasmine lactone (inset: $MS^3$ spectrum of $m/z$ 186).

which is a major type of involatile chalcone (flavonoid) of citrus.

Similarly, the ion of $m/z$ 153 was assigned to protonated vanillin. Upon CID, protonated vanillin cleaved $H_2O$ and CO to yield fragments of $m/z$ 135 and $m/z$ 125, respectively, which was consistent with the $MS^n$ result of vanillin standard obtained by MPT-MS. Because vanillin is a major flavor compound in orange fruits, it was quantitatively determined by using the external standard method.[39] As the result, the relative standard deviation (RSD) for vanillin in exocarp was 1.7%, and the limit of detection (LOD) was 0.119 $\mu$g/L. Quantitative analysis of the curve is $y = 177.7x - 5158$, $R^2 = 0.998$. The content order of vanillin for the navel oranges from these three habitats is Guoxi > Fengxi > Anxi.

Jasmine lactone (MW 168) is a natural compound providing sweet, flowery, and fruity flavors. In our case, the peaks at $m/z$ 169 and 186 were detected in the full-scan mass spectra of exocarp samples (Figure 5A–C). Subjection of $m/z$ 169 to CID resulted in the formation of $m/z$ 151, 141, 127, 109, and 95 by the loss of ($H_2O$), (CO), ($COCH_2-$), ($-CH_3COOH$), and ($-CH_3CH_2COOH$), respectively, which had the fragmentation pattern similar to that in the GC–MS analysis of jasmine lactone.[40] According to previous reports,[41,42] the peaks at $m/z$ 169 and 186 were the signs of jasmine lactone when analyzing gardenia and fruits of citrus. Thus, the detection of the peak at $m/z$ 186 (Figure 5A–C) also indicated the existence of jasmine lactone in navel orange exocarp samples. Therefore, the peak at $m/z$ 169 was tentatively identified as protonated jasmine lactone. The peak at $m/z$ 186 was probably the protonated product of jasmine lactone after hydrolysis, **4** (Figure 3). During the CID process, the precursor ion ($m/z$ 186) generated peaks at $m/z$ 168, 158, 144, 126, and 112 by the loss of ($H_2O$), (CO), ($COCH_2-$), ($-CH_3COOH$), and ($-CH_3CH_2COOH$) (Figure 6B), respectively. Note that the ion of $m/z$ 186 and the $MS^2$ ion of $m/z$ 168 (Figure 6B, inset) may have a fragmentation pattern similar to that of protonated jasmine lactone ($m/z$ 169), although the hydrolysis might affect the fragmentation pattern of the lactone. The small peak at $m/z$ 155 was ascribed to protonated nerol or geraniol, which is widespread in Rutaceae.[43,44]

More interestingly, a group of peaks at $m/z$ 343, 373, 403, and 433 corresponding to polymethoxyflavones (PMFs) appeared in the spectrum (Figure 5D) when the navel orange exocarp was heated by MPT for more than 30 s. The detection of PMFs was confirmed by comparing the multiple-stage tandem mass spectra (Table 1) with the $MS^n$ results in previous studies.[45,46] It was worth noting that few peaks were detected in the low mass range accompanying the PMFs, because the small analytes with a low mass-to-charge ratio were of high volatility and were almost evaporated before the PMFs were desorbed by MPT. For reference, only a few peaks rather than the PMFs at lower mass range were detected by DAPCI-MS,[47] indicating that the heating process facilitated by MPT was necessary for PMFs detection. More specifically, the peaks at $m/z$ 343, 373, 403, and 433 corresponded to tetramethyl-*o*-scutellarein, **5**, sinensetin, **6**, nobiletin, **7**, and 3,5,6,7,8,3′,4′-heptamethoxyflavone, **8** (Figure 3), respectively.[47] In the CID spectrum, their fragmentation patterns are consistent with each other by the loss of 15, 30, and 61 Da, corresponding to ($CH_3-$), ($CH_2O-$), and ($2CH_3O - H$), respectively.[47] Table 1 summarizes the CID data and signal intensity levels of the PMFs. As shown in Table 1, the signal intensity levels of $m/z$ 343, 403, and 433, which corresponded to 991 000, 2 030 000, and 758 000 cps, respectively, in Fengxi navel oranges were the highest among the three types of navel oranges. For sinensetin ($m/z$ 373), the signal intensity level in Fengxi navel oranges was only slightly lower than that in Anxi. In general, the content of PMFs was rich in Fengxi navel oranges. As the bioactive plant components in the orange peels, PMFs can be used to inhibit the growth of a variety of cancer cells, mutant cells, and to reduce the oxygen stress of cells. Presumably, the higher content of PMFs in fruits would bring more benefit to consumers. Therefore, as indicated in Table 1, the level of nobiletin was found to be highest in Fengxi navel oranges. The

**Table 1. Polymethoxyflavones Fragments and Signal Intensity Levels of Navel Orange Exocarp Samples**

| | | | | intensity | | |
|---|---|---|---|---|---|---|
| structure number | name | $m/z$ | main fragments | Guoxi | Anxi | Fengxi |
| **5** | tetramethyl-*O*-scutellarein | 343 | 328, 313, 299, 282 | 964000 | 935000 | 991000 |
| **6** | sinensetin | 373 | 358, 343, 329, 312 | 1500000 | 1840000 | 1830000 |
| **7** | nobiletin | 403 | 388, 373, 355, 342, 327 | 1500000 | 1860000 | 2030000 |
| **8** | 3,5,6,7,8,3′,4′-heptamethoxyflavone | 433 | 418, 403, 385, 372, 342 | 528000 | 696000 | 758000 |
| total/intensity | | | | 4490000 | 5330000 | 5600000 |



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detection of PMFs demonstrated that, assisted by heating, MPT favored desorption/ionization of typical nonvolatile compounds embedded even deeply in plant tissue, which might not be detectable using other ionization techniques such as DAPCI or DESI due to the lack of heating for efficient desorption.

**Visualization of the Differences among Navel Oranges.** The MS fingerprints of navel orange juice sacs (Figure 2) and exocarp (Figure 5) showed notable differences for the navel oranges cultivated in the three habitats. To easily visualize the recognition, a multivariate statistic tool, principal component analysis (PCA), was employed to process the MS fingerprints data.[48] For example, Figure 7A shows the PCA

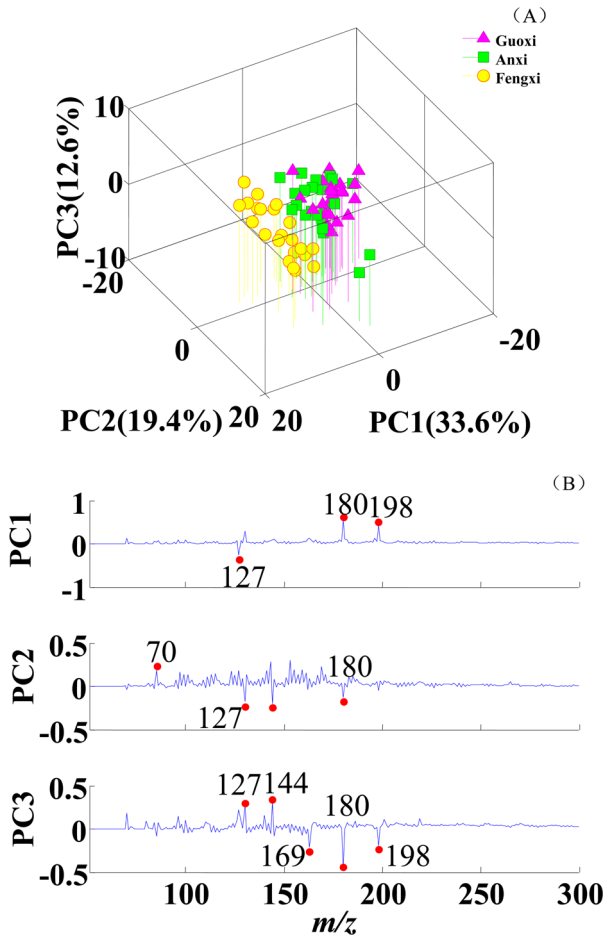


**Figure 7.** PCA score results of navel orange juice sac composition: (A) 3D-PCA score plot; and (B) PCA loading plots.

score plots obtained using MPT-MS with 72 individual juice sac samples, in which the samples collected from Fengxi were separated from those cultivated in either Guoxi or Anxi habitat. The Anxi navel oranges were almost as uniformly distributed in the 3-D PCA score plots as the Guoxi samples, showing that no significant difference was detected by MPT-MS from the juice sac samples, although the samples were cultivated in two habitats located in vicinity. The loading plots shown in Figure 7B indicated that sugars were the major differential ingredients among the navel oranges tested.

Similar to Figure 7A, the 72 navel oranges from Fengxi were clearly separated from the rest of the samples (Figure 8A) when PCA was applied to processing the MPT-MS fingerprints of

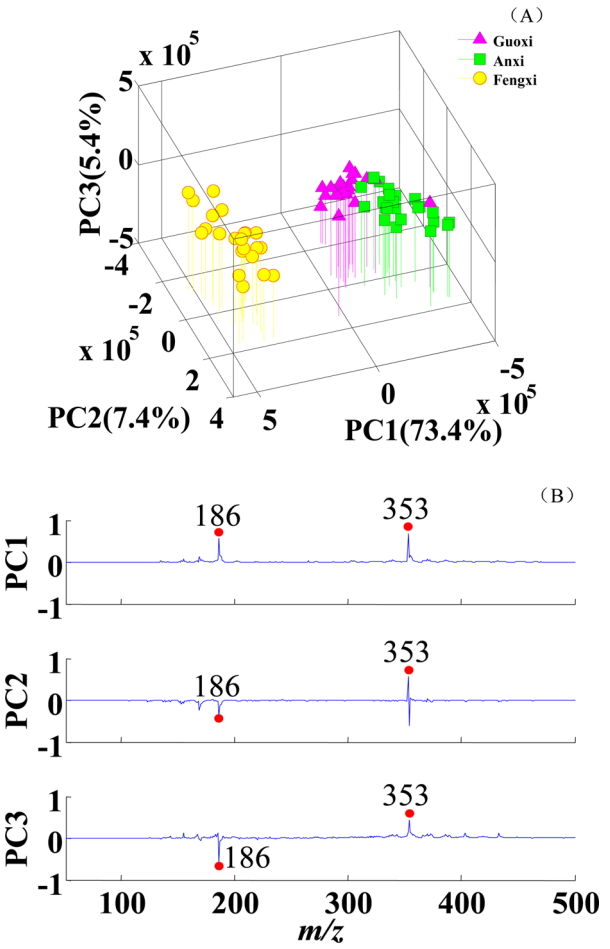


**Figure 8.** PCA score results of navel orange exocarp composition: (A) 3D-PCA score plot; and (B) PCA loading plots.

navel orange exocarp samples. However, both the Guoxi samples and the Anxi samples were tightly clustered in Figure 8A, resulting in better separation of the three types of navel orange samples. The improved differentiation was achieved by the differential analytes, that is, the major signals of citrunobin ($m/z$ 353) and hydrolysis product of jasmine lactone ($m/z$ 186) in the loading plots (Figure 8B), which were quite different from those shown in Figure 7B. Overall, the exocarp samples were better than the juice sacs samples for MPT-MS differential analysis of navel oranges cultivated in closely located habitats, providing easy access, fast analysis speed, and satisfactory differentiation.

In conclusion, the volatile aroma compounds such as vanillin, and semivolatile chemicals such as sugars, alcohols, and anticancer flavonoids in the juice sacs and exocarps of navel oranges, were sensitively detected by microwave plasma torch desorption ionization mass spectrometry (MPT-MS) followed by the statistical data analysis. Fast recognition of the quality and origin of fruits produced in three closely located habitats (Guoxi, Anxi, and Fengxi) was successfully achieved. The differentiation quality was notably improved by using MPT-MS data recorded from navel orange exocarp samples rather than the juice sac samples. The data thus demonstrate that MPT-MS is a sensitive analytical technique to reveal the differential information at the molecular level without invasive sample manipulation and is a promising method to allow distinction between the same types grown in neighboring vicinities.


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## ■ ASSOCIATED CONTENT

### Supporting Information

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Tandem mass spectra of vanillin and jasmine lactone in the navel oranges by MPT-MS; tandem mass spectra of 5-HMF standard, 1-nonanol standard, and vanillin standard obtained by MPT-MS; tandem mass spectra of the PMFs in the navel oranges by MPT-MS; and the RSD, LOD, and quantitative analysis curve of vanillin (PDF)

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### Notes

The authors declare no competing financial interest.

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